A SUMMARY OF THE DUVAL MASSIVE SULFIDE DEPOSIT, MARINETTE COUNTY, WISCONSIN

by

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ABSTRACT

The Duval Deposit in west-central Marinette County, Wisconsin, is a conformable, pyrrhotite-rich, massive sulfide lens that contains only trace amounts of base and precious metals. It occurs in an amphibolite facies submarine volcanic sequence that was characterized by calcalkaline basic flows, tuffs, iron formation and carbonaceous clastic sediments. The stratigraphy near the sulfide unit consists, from bottom to top, of: 1) interlayered massive basalt flows, basic tuffs and thin sulfidic carbonate iron formation, 2) a sulfidic iron formation that is overlain by the massive sulfide, and 3) graphitic mudstones and siltstones. The massive sulfides separate an upper marine clastic sedimentary sequence from a lower submarine volcanic and iron formation sequence.

Lack of unambiguous evidence for a footwall feeder conduit and absence of significant metal zoning are compatible with deposition of the graphitic sulfide mass in a distal or sedimentary basin rather than proximal to a volcanic center. The Eh-pH-f_{S_2} conditions did not favor precipitation of base metal sulfides; consequently copper and zinc sulfides are present only in trace amounts.

INTRODUCTION

The Duval Corporation conducted geological, geophysical and pilot exploratory drilling programs from 1971 through 1974 on an unexposed conformable massive sulfide body at 88° 14' W, 45° 35' N (sec. 2 and 3, T.35N., R. 18E. and Sec. 28, T.36N., R. 18E) in west-central Marinette County, Wisconsin. The deposit, which contains mainly iron sulfide, is referred to as the Duval Deposit by the mining industry and was discovered by airborne geophysical methods. The massive sulfide layer occurs in the Precambrian rocks of northeastern Wisconsin in a layer up to 30 m thick. Drilling suggests the deposit contains on the order of 10 million tons of sulfide-rich material that could supply 3 million tons of recoverable sulfur. At present, however, neither metallic nor nonmetallic reserves have been proven. Pertinent technical data, including geologic, geochemical, drill data, and core, for the deposit were given to the Wisconsin Geological and Natural History Survey and the University of Wisconsin (Cummings, 1978) and are available to the public.

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The Duval cores are part of the Survey collection of drill cores which are available for public inspection at the core repository in Milwaukee during the first full work week of each month. For additional information on the cores collection, or on the core repository, please contact the Exploration records Specialist at the Wisconsin Geological and Natural History Survey (608/262-1705).

The Duval sulfide deposit differs from other known large massive sulfide deposits in Wisconsin. It is nearly devoid of base and precious metals; it separates a dominantly basic submarine volcanic and iron formation footwall assemblage from a hangingwall marine clastic sequence; and it occurs with sulfidic carbonate iron formation. This paper briefly describes the Duval deposit and considers why the Duval massive sulfide, unlike the Kennecott (May, 1977), Noranda (Mudrey, 1979) and Exxon (Schmidt and others, 1978) discoveries, is barren of significant copper, zinc and lead. Careful documentation of the geology of sub-economic deposits and comparison to economic deposits may provide valuable clues to differences in the systems that formed the deposits and provide useful information to guide exploration for economic deposits.

The data on which the following sections are based can be found in Cummings (1978).

GEOLOGIC SETTING

The Duval massive sulfide deposit occurs in the Lower Proterozoic volcanic rocks of west-central Marinette County, Wisconsin (Fig. 1). The volcanic rocks have been included in the Quinnesec Formation (Cummings, 1978). The Quinnesec Formation is a name generally applied to those mafic volcanic rocks of Dickinson County, Michigan and adjoining northeastern Wisconsin. Recent work (Cummings, 1980) on the petrochemistry of the volcanic rocks indicates that they are dissimilar to the Quinnesec Formation as sampled in the area defined as Quinnesec Formation by Jenkins (1973) and chemically analyzed by Cudzilo (1978). In the vicinity of the Duval Deposit, the volcanics are composed of basic submarine volcanic, volcaniclastic and sedimentary rocks. Although Banks and Rebello (1969) reported U-Pb ages on zircon from a rhyolite east of the massive sulfide deposit in what was believed to be the Quinnesec Formation, the age of the mafic rocks associated with the deposit remains unknown. The volcanics are bounded by 1860 to 1890 m.y. old granitic plutons (Banks and Cain, 1979, Van Schmus and others, 1975). Cummings (1978) concluded from mineralogy that metamorphism of the deposit occurred at amphibolite grade and that peak temperature of 540° C and maximum pressure of 3.5 kb was reached during metamorphism.

The volcanic sequence in west-central Marinette County consists of massive and fragmental basalt, andesite, dacite and rhyolite flows, tuffs, volcaniclastic, clastic and chemical sedimentary rocks. The flow units represent an orogenic calcalkaline suite. The massive sulfide deposit occurs in sedimentary units that appear to have been deposited some distance from a major volcanic center in a sedimentary basin characterized by chemical sedimentation, fine-grained graphitic clastic sediments and quiet, probably deep water.

The stratigraphic relations of the sulfide unit has been defined from drill core since the unit does not crop out. Sparse top indicators in core samples suggest that the units are folded about an anticlinal axis that plunges gently to the southeast (Fig. 2). The limbs of the anticline are steeply dipping. Since the drill holes were drilled to the south on the north limb and

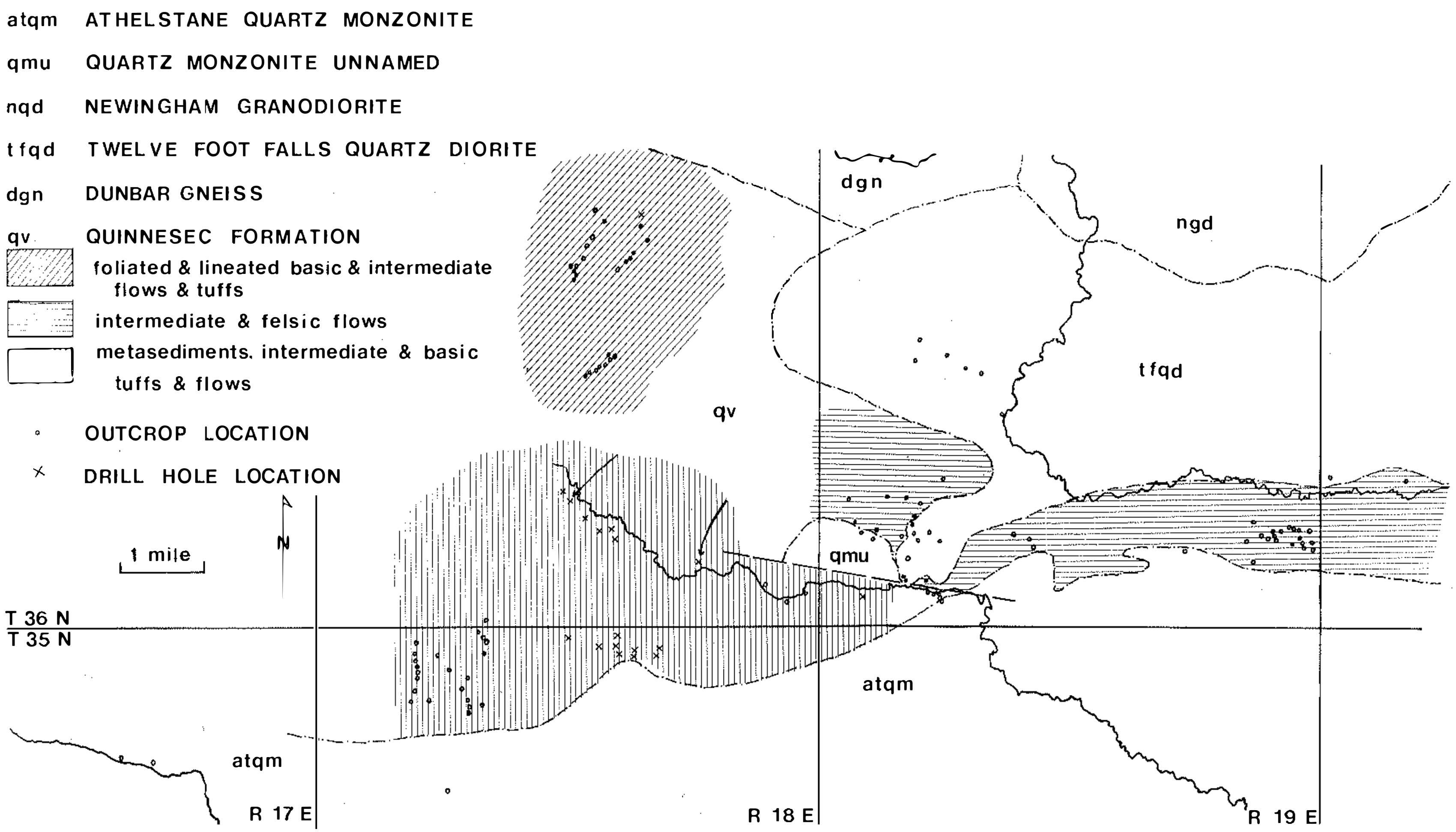

Figure 1. Generalized geologic map of west-central Marinette County, Wisconsin.

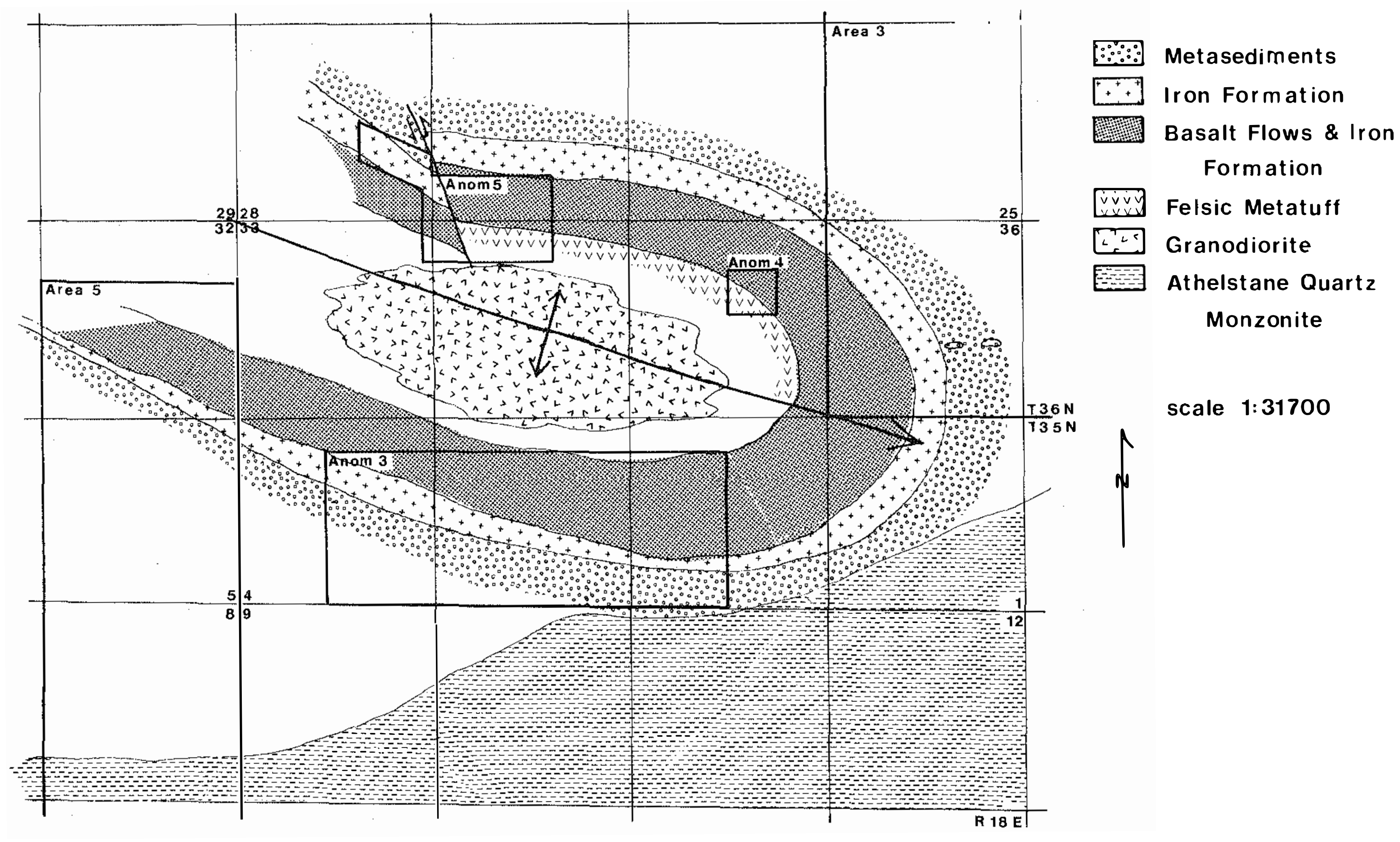

Figure 2. Geologic interpretation of an anticline in the area of the Duval deposit.

to the north on the south limb of the anticline, the rocks at the bottom of the holes are believed to be the oldest units. The stratigraphy associated with the Duval massive sulfide includes approximately 220 m of massive basalt flows, interflow basic tuffs and thin layers of sulfidic carbonate iron formation. The basalt flow unit is overlain by a sulfidic carbonate iron formation lens that varies in thickness from 10 to 40 m. Massive to semi-massive graphitic sulfide in a bed up to 30 m thick conformably overlies the iron formation and in turn is conformably overlain by graphitic mudstones and well-bedded siltstones. Sulfide minerals comprise less than 5 percent of the upper sedimentary unit.

DESCRIPTION OF ROCK UNITS

Basalt Flow Unit

Basalt flows are the main rock type in the unit. The flows are from 1- to 60-m thick and are massive. The textural relations between hornblende and plagioclase preserves a relict sub-ophitic texture in most flows. Each flow is generally overlain by faintly bedded basic tuff. The tuffs commonly contain beds up to 2-mm thick that are greater than 60 percent epidote. Besides epidote, the mineralogy of the tuffs includes actinolitic hornblende, chlorite and minor plagioclase. The mineralogy suggests basic ash contaminated by carbonate. The basic tuffs grade stratigraphically into sulfidic carbonate iron formation. Iron formation lenses can be as much as 1-m thick and contain up to 20 percent sulfide. Pyrrhotite, with traces of chalcopyrite, pyrite and sphalerite are disseminated in some amphibole-rich beds.

Iron Formation Unit

The iron formation lenses in the volcanic sequence are believed to represent metamorphosed carbonate-chert iron formation. Under metamorphic conditions of the amphibolite facies, the carbonate has apparently reacted with silica to produce interlayered quartz and iron-amphibole beds. The iron amphiboles, the main phases in the iron formation, are overwhelmingly grunerite with minor to trace amounts of ferro-actinolite and ferro-hornblende. The carbonate, present in trace amounts, is calcite. Garnet and stilpnomelane are locally present. The composition of the iron-rich beds is basically represented by the composition of the grunerite which ranges from 31 to 45 weight percent FeO (Cummings, 1978). Where magnetite is present the weight percent of FeO in grunerite is lower and cummingtonite may occur as the main amphibole (amphibole classifications are according to the Subcommittee on Amphiboles, IMA, Leake, 1978).

The iron formation unit was divided by Cummings (1978) into an upper and lower member. The lower member is characterized by pyrrhotite beds to 2-mm thick, but sparse sulfide beds may reach 10 cm in thickness. Traces of chalcopyrite and sphalerite are megascopically visible in some beds. The upper member contains stilpnomelane with grunerite, and garnet-graphite-quartz beds become common. Sulfide minerals are finely disseminated in iron silicate beds except in the upper part of the member where sulfides are interbedded with quartz beds. The sulfide beds become more abundant toward the top of the unit. Magnetite is most abundant (greater than 10 percent) in the upper part of the lower member and lower part of the upper member. Ilmenite, determined by microprobe analyses, is the oxide phase in some beds.

Massive Sulfide Unit

The percentage of sulfide in the upper part of the iron formation unit increases and becomes semi-massive (10- to 40-percent sulfide). The sulfides are well bedded, however in the main sulfide zone the sulfide forms a matrix between fragments of polycrystalline quartz and graphitic lithic sediments. In the main zone the sulfide is semi-massive to massive. The main sulfide mineral is pyrrhotite; pyrite is rare and sphalerite and chalcopyrite occur in trace amounts. Zoning of metal values has not been noted in the deposit and lateral persistence of internal textures, structures or composition have not been shown. Drill intercepts indicate thicknesses from 3 m to 20 m for the fragmental unit along a strike length of at least 1300 m. The fragmental unit is considered a sulfur resource that contains roughly 10 million tons of sulfide ore. If the semi-massive sulfide layers in the iron formation are included in the resource estimate the tonnage approaches 40 million tons.

Magnesium-rich silicate assemblages underlie the sulfide unit and are texturally and structurally similar to the sulfide-rich upper iron formation member. Such magnesium-rich silicates are noted at least 5 m below the base of the main sulfide unit but may locally be absent. Bedding structures in the materials are similar to those in iron formation even though the mineralogy is tremolite and muscovite rather than iron silicates. Fragmental textures in an apparent basic crystal tuff are preserved in an assemblage containing anthophyllite and Mg-Fe chlorite.

Mudstone and Siltstone Unit

Well-bedded clastic sediments overlie the massive sulfide unit. The sediments immediately above the sulfide unit are highly graphitic and fine grained. Folds in the unit are believed to represent soft-sediment deformation features. The amount of graphite decreases upward as the grain size becomes coarser until the unit is a graphitic, well-bedded siltstone. Pyrrhotite and minor pyrite form thin beds in the mudstone and siltstone and range to 5 percent as disseminated grains in thin hornblende-epidote-plagioclase beds that may represent basic tuffs.

DISCUSSION

The Duval Deposit appears to have been deposited in a chemically reducing, sedimentary basin that was not in the immediate vicinity of a volcanic center. Plimer (1978) suggested several characteristics that distinguish stratabound deposits formed at varying distances from volcanic centers. The deposits formed near the center, called proximal deposits, occur in intermediate to acid explosive volcanic rocks in parts of the volcanic pile where the proportion of lavas and pyroclastic rocks to sediments is high. Alteration pipes, stringer sulfide zones and disseminated sulfides are common in the footwall of the proximal deposits. The deposits formed away from a center, or distal deposits, are found in areas where there is a high proportion of clastic and chemical sediments to pyroclastic rocks and lava flows. There is no clear spatial relation of the deposit to a footwall alteration pipe or stringer zone. In terms of the associated stratigraphy, the Duval Deposit is a distal deposit, however the origin of the Mg-rich zone beneath the sulfide unit is not clear and must be considered.

There are three possible origins for the magnesium-rich zone: 1) a metamorphosed dolomitic cherty tuff as protolith for the tremolite-bearing rocks. 2) a metamorphosed epigenetic feeder pipe that owes magnesium enrichment to metasomatism during sea floor hot spring activity, or 3) the effects of metamorphic reactions in the immediate vicinity of the sulfide-silicate unit contact. The available data do not allow a clear choice among the three possible origins.

The mineral assemblages of the zones contain high magnesium phases and are in marked compositional contrast to underlying iron formation. The Mg/(Mg + Fe) ratios for tremolite are 0.98 and are 0.90 for associated chlorite. The iron-bearing phases are sulfides and tourmaline has been noted in one assemblage. The anthophyllite-bearing assemblage is more iron-rich. The Mg/(Mg +Fe) ratio for anthophyllite is approximately 0.82 and 0.55 for associated chlorite. The proposed origin for the zone must be consistent with these facts.

The first proposed origin suggests a sedimentary protolith for the deposits. A siliceous dolomite mixed with volcanic ash or clays might be the parent material for the tremolite-bearing assemblages. The suggested protolith would indicate depositional change from siderite + chert to dolomite + chert to massive sulfide + chert upward in the stratigraphic sequence. Such associations of various carbonate phases and massive sulfide deposits have been noted in pyrrhotite and pyrrhotite + pyrite massive sulfide units recorded in Rhodesia where carbonate units from iron formation to limestones are closely associated with massive sulfide deposits (Anhaeusser and Ryan, 1976). Although a parent rock can be proposed, there are problems with the interpretation. The replacement textures in the basic tuff bed that now contains anthophyllite and chlorite are not explained by the sedimentary model. Also the irregular thickness of the magnesium-rich zone does not seem consistent with a sedimentary model. The zones may be absent in some holes and at least 5-m thick in others, suggesting possible discordant relations to the enclosing stratigraphy.

The replacement textures in the basic tuffs and possible replacement of iron formation by the tremolite assemblages suggest alteration of sediment by metasomatic activity. Plimer (1978) suggested that alteration associated with distal massive sulfide deposits should show slight increases in K_2O, FeO, MnO, TiO_2 and SiO_2 and slight decreases in Na_2O, CaO and MgO. The tremolite assemblages suggest MgO and CaO may have been added to the rock rather than subtracted. The composition and mineralogy of the assemblage does not appear consistent with the compositions and mineralogies of known alteration zones associated with massive sulfide deposits (Simmons, 1973; Gilmour, 1965; Spence and Rosen-Spence, 1975; Kelly, 1975; Walker and others, 1975; Roberts, 1975; Franklin and others, 1975).

The third possible origin, metamorphogenic processes, is suggested by the effects of sulfurization reactions or fluid phase reactions during metamorphism. This interpretation would indicate that the magnesium-rich bulk composition was established during metamorphism. A magnesium-rich silicate assemblage can be produced by sulfurization reactions at elevated temperatures (Bischoff and Dickson, 1975), however, the reactions should produce calcium-poor assemblages since calcium is enriched in the vapor phase. Also, if the magnesium-rich materials were produced by sulfurization reactions, then the sulfide minerals would probably not show a bedded pattern. The circulation of fluids during metamorphism has been suggested as a mechanism to produce alteration zones around the deposits at Ducktown, Tennessee (Abby and Yuma, 1977). In the model, trace sedimentary sulfide was remobilized during regional metamorphism and the sulfide was deposited by hydrothermal solutions in shear zones. The alteration zones around the ore bodies occurred late during the matamorphism as water continued to pass through the shear zones in which the deposits occur. There is neither evidence for sulfide deposition in shear zones nor alteration surrounding the Duval Deposit. The magnesium-rich assemblages are only in the footwall of the deposit.

Although the three proposed models for the origin of the magnesium-rich zones associated with the Duval Deposit can be supported by some data, the models either cannot explain all the features of the zones or are apparently contradicted by features in the zones.

The physical-chemical environment of sea water at the time of deposition is reflected in the chemical sediments that form. Eh, pH and f_{S_2} would affect either magnetite, magnetite-pyrrhotite or pyrrhotite deposition in the bed. The increasing proportion of pyrrhotite rather than magnetite upward in the iron formation suggests steadily increasing f_{S_2}, possibly the result of increased biological activity.

If the Eh, pH and f_{S_2} conditions remained close to the boundary for coprecipitation of pyrrhotite and magnetite, then there was a limited likelihood of chalcopyrite and sphalerite deposition (Large, 1977). The concentration of copper and zinc in seawater as the Duval Deposit was formed cannot be known, however, the presence of chalcopyrite and sphalerite in iron formation and massive sulfide, although not exceeding 0.5 percent irrespective of the percentage of sulfide in the rock, indicates the presence of metals during the depositional process. Thus, the lack of base metals in the iron formation and sulfide units may have been a result of non-deposition due to environmental conditions rather than a lack of base metals in seawater.

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